

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C11D 3/40, 17/04	A1	(11) International Publication Number: WO 97/26315 (43) International Publication Date: 24 July 1997 (24.07.97)
(21) International Application Number: PCT/US97/00812 (22) International Filing Date: 7 January 1997 (07.01.97) (30) Priority Data: 08/588,667 18 January 1996 (18.01.96) US 08/628,436 5 April 1996 (05.04.96) US (71) Applicant: COLGATE-PALMOLIVE COMPANY [US/US]; 300 Park Avenue, New York, NY 10022 (US). (72) Inventors: JAKUBICKI, Gary; 7 Milburne Lane, Robbinsville, NJ 08691 (US). GOMES, Gilbert, S.; 282 Abbey Drive, Somerset, NJ 08873 (US). URAY, Alp; 42 S. Ross Hall Boulevard, Piscataway, NJ 08854 (US). (74) Agent: NANFELDT, Richard; Colgate-Palmolive Company, 909 River Road, Piscataway, NJ 08855-1343 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: FILLED PACKAGE OF LIGHT DUTY LIQUID CLEANING COMPOSITION (57) Abstract The present invention relates to a filled package comprising a tinted or untinted transparent container and a tinted liquid cleaning composition contained in the container.		

10/772824



020504

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

FILLED PACKAGE OF LIGHT DUTY LIQUID CLEANING COMPOSITION**Related Application**

This application is a continuation in part application of U.S. Serial No. 8/588,667
5 filed 1/18/96.

Field of Invention

This invention relates to filled package of a tinted or untinted bottle containing a light duty liquid cleaning composition which is transparent and is colorless or slightly blue/green or slightly green/yellow.

10 Background of the Invention

In recent years all-purpose liquid detergents have become widely accepted for cleaning hard surfaces, e.g., painted woodwork and panels, tiled walls, wash bowls, bathtubs, linoleum or tile floors, washable wall paper, etc. Such all-purpose liquids comprise clear and opaque aqueous mixtures of water-soluble synthetic organic
15 detergents and water-soluble detergent builder salts. In order to achieve comparable cleaning efficiency with granular or powdered all-purpose cleaning compositions, use of water-soluble inorganic phosphate builder salts was favored in the prior art all-purpose liquids. For example, such early phosphate-containing compositions are described in U.S. Patent Nos. 2,560,839; 3,234,138; 3,350,319; and British Patent No. 1,223,739.

20 In view of the environmentalist's efforts to reduce phosphate levels in ground water, improved all-purpose liquids containing reduced concentrations of inorganic phosphate builder salts or non-phosphate builder salts have appeared. A particularly useful self-opacified liquid of the latter type is described in U.S. Patent No. 4,244,840.

25 However, these prior art all-purpose liquid detergents containing detergent builder salts or other equivalent tend to leave films, spots or streaks on cleaned unrinsed surfaces, particularly shiny surfaces. Thus, such liquids require thorough rinsing of the cleaned surfaces which is a time-consuming chore for the user.

In order to overcome the foregoing disadvantage of the prior art all-purpose liquid, U.S. Patent No. 4,017,409 teaches that a mixture of paraffin sulfonate and a

reduced concentration of inorganic phosphate builder salt should be employed. However, such compositions are not completely acceptable from an environmental point of view based upon the phosphate content. On the other hand, another alternative to achieving phosphate-free all-purpose liquids has been to use a major proportion of a mixture of anionic and nonionic detergents with minor amounts of glycol ether solvent and organic amine as shown in U.S. Patent No. 3,935,130. Again, this approach has not been completely satisfactory and the high levels of organic detergents necessary to achieve cleaning cause foaming which, in turn, leads to the need for thorough rinsing which has been found to be undesirable to today's consumers.

Another approach to formulating hard surface or all-purpose liquid detergent composition where product homogeneity and clarity are important considerations involves the formation of oil-in-water (o/w) microemulsions which contain one or more surface-active detergent compounds, a water-immiscible solvent (typically a hydrocarbon solvent), water and a "cosurfactant" compound which provides product stability. By definition, an o/w microemulsion is a spontaneously forming colloidal dispersion of "oil" phase particles having a particle size in the range of about 25 to about 800 Å in a continuous aqueous phase.

In view of the extremely fine particle size of the dispersed oil phase particles, microemulsions are transparent to light and are clear and usually highly stable against phase separation.

Patent disclosures relating to use of grease-removal solvents in o/w microemulsions include, for example, European Patent Applications EP 0137615 and EP 0137616 - Herbots et al; European Patent Application EP 0160762 - Johnston et al; and U.S. Patent No. 4,561,991 - Herbots et al. Each of these patent disclosures also teaches using at least 5% by weight of grease-removal solvent.

It also is known from British Patent Application GB 2144763A to Herbots et al, published March 13, 1985, that magnesium salts enhance grease-removal performance of organic grease-removal solvents, such as the terpenes, in o/w microemulsion liquid

detergent compositions. The compositions of this invention described by Herbots et al. require at least 5% of the mixture of grease-removal solvent and magnesium salt and preferably at least 5% of solvent (which may be a mixture of water-immiscible non-polar solvent with a sparingly soluble slightly polar solvent) and at least 0.1% magnesium salt.

However, since the amount of water immiscible and sparingly soluble components which can be present in an o/w microemulsion, with low total active ingredients without impairing the stability of the microemulsion is rather limited (for example, up to about 18% by weight of the aqueous phase), the presence of such high quantities of grease-removal solvent tend to reduce the total amount of greasy or oily soils which can be taken up by and into the microemulsion without causing phase separation.

The prior art is replete with light duty liquid detergent compositions containing nonionic surfactants in combination with anionic and/or betaine surfactants. U.S. Patent No. 3,769,398 discloses a betaine-based shampoo containing minor amounts of nonionic surfactants. This patent states that the low foaming properties of nonionic detergents renders its use in shampoo compositions non-preferred. U.S. Patent No. 4,329,335 also discloses a shampoo containing a betaine surfactant as the major ingredient and minor amounts of a nonionic surfactant and of a fatty acid mono- or di-ethanolamide. U.S. Patent No. 4,259,204 discloses a shampoo comprising 0.8-20% by weight of an anionic phosphoric acid ester and one additional surfactant which may be either anionic, amphoteric, or nonionic. U.S. Patent No. 4,329,334 discloses an anionic-amphoteric based shampoo containing a major amount of anionic surfactant and lesser amounts of a betaine and nonionic surfactants.

U.S. Patent No. 3,935,129 discloses a liquid cleaning composition based on the alkali metal silicate content and containing five basic ingredients, namely, urea, glycerin, triethanolamine, an anionic detergent and a nonionic detergent. The silicate content determines the amount of anionic and/or nonionic detergent in the liquid

+

cleaning composition. However, the foaming property of these detergent compositions is not discussed therein.

U.S. Patent No. 4,129,515 discloses a heavy duty liquid detergent for laundering fabrics comprising a mixture of substantially equal amounts of anionic and nonionic
5 surfactants, alkanolamines and magnesium salts, and, optionally, zwitterionic surfactants as suds modifiers.

U.S. Patent No. 4,224,195 discloses an aqueous detergent composition for laundering socks or stockings comprising a specific group of nonionic detergents, namely, an ethylene oxide of a secondary alcohol, a specific group of anionic
10 detergents, namely, a sulfuric ester salt of an ethylene oxide adduct of a secondary alcohol, and an amphoteric surfactant which may be a betaine. wherein either the anionic or nonionic surfactant may be the major ingredient.

The prior art also discloses detergent compositions containing all nonionic surfactants as shown in U.S. Patent Nos. 4,154,706 and 4,329,336 wherein the
15 shampoo compositions contain a plurality of particular nonionic surfactants in order to effect desirable foaming and deterative properties despite the fact that nonionic surfactants are usually deficient in such properties.

U.S. Patent No. 4,013,787 discloses a piperazine based polymer in conditioning and shampoo compositions which may contain all nonionic surfactant or all anionic
20 surfactant.

U.S. Patent 4,671,895 teaches a liquid detergent composition containing an alcohol sulfate surfactant, a nonionic surfactant, a paraffin sulfonate surfactant, an alkyl ether sulfate surfactant and water.

U.S. Patent No. 4,450,091 discloses high viscosity shampoo compositions
25 containing a blend of an amphoteric betaine surfactant, a polyoxybutylene polyoxyethylene nonionic detergent, an anionic surfactant, a fatty acid alkanolamide and a polyoxyalkylene glycol fatty ester. But, none of the exemplified compositions contains an active ingredient mixture wherein the nonionic detergent is present in major

proportion, probably due to the low foaming properties of the polyoxybutylene polyoxyethylene nonionic detergent.

U.S. Patent No. 4,595,526 describes a composition comprising a nonionic surfactant, a betaine surfactant, an anionic surfactant and a C₁₂-C₁₄ fatty acid monethanolamide foam stabilizer.

However, none of the above-cited patents discloses a filled package of a tinted or untinted bottle containing a liquid cleaning composition which appears transparent and is colorless or slightly blue/green or slightly green/yellow.

Summary of the Invention

The present invention relates to a transparent blue or violet tinted cleaning liquid disposed in a blue or violet tinted or untinted transparent container such as a bottle wherein the cleaning composition comprises approximately by weight:

(a) 0.05% to 50%, more preferably 0.1% to 30% of at least one surfactant selected from the group consisting of sulfonate surfactants, alkyl sulfate surfactants, ethoxylated alkyl ether surfactants, glucamide surfactants, zwitterionic surfactants, alkyl glucoside surfactants, alkyl polyglucoside surfactants, amine oxide surfactants, nonionic surfactants containing ethylene oxide groups and mono- and/or di-alkanol amides and mixture thereof;

(b) 10 to 3000 ppb, more preferably 100 to 1,400 ppb of a violet or blue dye; and

(c) the balance being water, wherein the liquid cleaning composition has chromaticity coordinate values of x from about 0.3080 to about 0.3240 and of y from about 0.3280 to about 0.3430, wherein the transparent container has chromaticity coordinate values of x from about 0.3080 to about 0.3240 and of y from about 0.3280 to about 0.3430 and the cleaning liquid composition taken together with the transparent container has chromaticity coordinate values of x from about 0.3100 to about 0.3200 and of y from about 0.3300 to about 0.3400.

An objective of the instant invention is a filled package of blue or violet tinted transparent liquid cleaning composition disposed in a transparent blue or violet tinted or

untinted container such that the appearance of the filled package is substantially transparent and neutral in color or slightly blue/green or slightly yellow/green in appearance.

Detailed Description of the Invention

5 The present invention relates to a filled package of a transparent blue or violet tinted liquid cleaning composition comprising 0.05 wt. % to 50 wt. %, more preferably 0.1 wt. % to 30 wt. % of at least one surfactant selected from the group consisting of alkyl sulfate surfactants, sulfonate surfactants, ethoxylated alkyl ether surfactants, glucamide surfactants, alkyl polyglucoside surfactants, amine oxide surfactants and
10 nonionic surfactants containing ethylene oxide groups and mixtures thereof; 10 to 3000 ppm, more preferably 100 to 1400 ppm of a blue or violet dye and the balance being water, wherein the liquid cleaning composition is disposed in a transparent blue or violet tinted container or transparent untinted container such as a glass or thermoplastic bottle selected from the group consisting of polyvinyl chloride, polystyrene, polyethylene or
15 polyethylene terephthalate.

 The transparent blue or violet tinted untinted containers such as a bottle in which the transparent liquid which has been tinted with a blue or violet fluorescent dye has chromaticity coordinates values of x from about 0.3080 to about 0.3240 and of y from 0.3280 to 0.3430. The liquid containing the fluorescent blue or violet fluorescent dye
20 has chromaticity coordinates values of x from about 0.3080 to about 0.3240 and of y from about 0.3280 to about 0.3430. The chromaticity coordinates values of the transparent container (untinted or tinted) with the transparent liquid containing the fluorescent blue or violet dye disposed in the transparent container is x from about 0.3100 to about 0.3200 and y from about 0.3300 to about 0.3400. The x and y values
25 were obtained from the tristimulus values (x, y and z) obtained from measurements made using a Macbeth 7000 using FMS-1, 10 degree observer, D65 illuminant at 25°C and calibrated BTIL = barium sulfate, transmission, specular ion, UV inc., large artic view. The color of the container and the color of the liquid containing the fluorescent blue or violet dye are not complimentary colors designed to cooperate to cancel each

other. The final color of the filled package which is the combination of the transparent container with the transparent liquid containing the fluorescent blue or violet dye will be neutral in appearance or slightly blue/green in appearance or slightly yellow/green in appearance. If the container is tinted with a blue or violet tint, the combination of the
5 blue or violet tinted bottle and blue or violet tinted liquid will be neutral in appearance or slightly blue/green in appearance.

The untinted container or untinted liquid are yellow/green in appearance having x values greater than about 0.3200 and y values greater than about 0.3400. The tinting of the bottle with a blue or violet tint and the tinting of the liquid with a blue or violet tint
10 permits neutralizing of the yellow/green color. Values of a and b CIELAB coordinates in the CIELAB system are:

- (a) transparent container a is from 0 to about -3 and b is from 0 to about -5;
- (b) fluorescent blue or violet tinted liquid cleaning composition a is from 0 to about -3.5 and b is from about 7 to about -5; and
- 15 (c) filled package container with blue or violet tinted liquid cleaning composition a is from 0 to about -3 and b is from about 7 to about -3, more preferably a is 0 to about -2.5 and b is about 3 to about -2.0.

The nonionic surfactant is present in amounts of about 0 to 30 wt. %, preferably 1 wt. % to 16 wt. % of the composition and provides superior performance in the
20 removal of oily soil and mildness to human skin. The water soluble nonionic surfactants utilized in this invention are commercially well known and include the primary aliphatic alcohol ethoxylates, secondary aliphatic alcohol ethoxylates, alkylphenol ethoxylates and ethylene-oxide-propylene oxide condensates on primary alkanols, such as Plurafacs (BASF) and condensates of ethylene oxide with sorbitan fatty acid esters such as the
25 Tweens (ICI). The nonionic synthetic organic detergents generally are the condensation products of an organic aliphatic or alkyl aromatic hydrophobic compound and hydrophilic ethylene oxide groups. Practically any hydrophobic compound having a carboxy, hydroxy, amido, or amino group with a free hydrogen attached to the nitrogen can be condensed with ethylene oxide or with the polyhydration product thereof.

polyethylene glycol, to form a water-soluble nonionic detergent. Further, the length of the polyethenoxy chain can be adjusted to achieve the desired balance between the hydrophobic and hydrophilic elements.

The nonionic surfactant class includes the condensation products of a higher alcohol (e.g., an alkanol containing about 8 to 18 carbon atoms in a straight or branched chain configuration) condensed with about 5 to 30 moles of ethylene oxide, for example, lauryl or myristyl alcohol condensed with about 16 moles of ethylene oxide (EO), tridecanol condensed with about 6 to moles of EO, myristyl alcohol condensed with about 10 moles of EO per mole of myristyl alcohol, the condensation product of EO with a cut of coconut fatty alcohol containing a mixture of fatty alcohols with alkyl chains varying from 10 to about 14 carbon atoms in length and wherein the condensate contains either about 6 moles of EO per mole of total alcohol or about 9 moles of EO per mole of alcohol and tallow alcohol ethoxylates containing 6 EO to 11 EO per mole of alcohol.

A preferred group of the foregoing nonionic surfactants are the Neodol ethoxylates (Shell Co.), which are higher aliphatic, primary alcohol containing about 9-15 carbon atoms, such as C₉-C₁₁ alkanol condensed with 7 to 10 moles of ethylene oxide (Neodol 91-8), C₁₂-13 alkanol condensed with 6.5 moles ethylene oxide (Neodol 23-6.5), C₁₂-15 alkanol condensed with 12 moles ethylene oxide (Neodol 25-12), C₁₄-15 alkanol condensed with 13 moles ethylene oxide (Neodol 45-13), and the like. Such ethoxamers have an HLB (hydrophobic lipophilic balance) value of about 8 to 15 and give good O/W emulsification, whereas ethoxamers with HLB values below 8 contain less than 5 ethyleneoxide groups and tend to be poor emulsifiers and poor detergents.

Additional satisfactory water soluble alcohol ethylene oxide condensates are the condensation products of a secondary aliphatic alcohol containing 8 to 18 carbon atoms in a straight or branched chain configuration condensed with 5 to 30 moles of ethylene oxide. Examples of commercially available nonionic detergents of the foregoing type are C₁₁-C₁₅ secondary alkanol condensed with either 9 EO (Tergitol 15-S-9) or 12 EO (Tergitol 15-S-12) marketed by Union Carbide.

Other suitable nonionic surfactants include the polyethylene oxide condensates of one mole of alkyl phenol containing from about 8 to 18 carbon atoms in a straight- or branched chain alkyl group with about 5 to 30 moles of ethylene oxide. Specific examples of alkyl phenol ethoxylates include nonyl phenol condensed with about 9.5 moles of EO per mole of nonyl phenol, dinonyl phenol condensed with about 12 moles of EO per mole of phenol, dinonyl phenol condensed with about 15 moles of EO per mole of phenol and di-isooctylphenol condensed with about 15 moles of EO per mole of phenol. Commercially available nonionic surfactants of this type include Igepal CO-630 (nonyl phenol ethoxylate) marketed by GAF Corporation.

Also among the satisfactory nonionic surfactants are the water-soluble condensation products of a C₈-C₂₀ alkanol with a heteric mixture of ethylene oxide and propylene oxide wherein the weight ratio of ethylene oxide to propylene oxide is from 2.5:1 to 4:1, preferably 2.8:1 to 3.3:1, with the total of the ethylene oxide and propylene oxide (including the terminal ethanol or propanol group) being from 60-85%, preferably 70-80%, by weight. Such detergents are commercially available from BASF-Wyandotte and a particularly preferred detergent is a C₁₀-C₁₆ alkanol condensate with ethylene oxide and propylene oxide, the weight ratio of ethylene oxide to propylene oxide being 3:1 and the total alkoxy content being about 75% by weight.

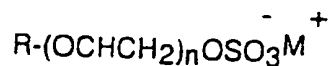
Condensates of 2 to 30 moles of ethylene oxide with sorbitan mono- and tri-C₁₀-C₂₀ alkanolic acid esters having a HLB of 8 to 15 also may be employed as the nonionic detergent ingredient in the described composition. These surfactants are well known and are available from Imperial Chemical Industries under the Tween trade name. Suitable surfactants include polyoxyethylene (4) sorbitan monolaurate, polyoxyethylene (4) sorbitan monostearate, polyoxyethylene (20) sorbitan trioleate and polyoxyethylene (20) sorbitan tristearate.

Other suitable water-soluble nonionic surfactants are marketed under the trade name "Pluronics." The compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The molecular weight of the hydrophobic portion of the molecule is of the order of 950

to 4000 and preferably 200 to 2,500. The addition of polyoxyethylene radicals to the hydrophobic portion tends to increase the solubility of the molecule as a whole so as to make the surfactant water-soluble. The molecular weight of the block polymers varies from 1,000 to 15,000 and the polyethylene oxide content may comprise 20% to 80% by weight. Preferably, these surfactants will be in liquid form and satisfactory surfactants are available as grades L 62 and L 64.

The alkyl sulfate surfactants which can be used in the instant compositions at a concentration of 0 to about 20 wt. %, more preferably about 0.5 to 15 wt. % are ammonium, alkali metal or alkaline earth metal salts of C₈-C₁₂ alkyl sulfates such as lauryl sulfate or myristyl sulfate. Ammonium lauryl sulfate is preferred.

The C₈-18 ethoxylated alkyl ether sulfate surfactants which can be used in the instant composition have the structure



wherein n is about 1 to about 22 more preferably 1 to 3 and R is an alkyl group having about 8 to about 18 carbon atoms, more preferably 12 to 15 and natural cuts, for example, C₁₂-14; C₁₂-15 and M is an ammonium cation, alkali metal or an alkaline earth metal cation, most preferably magnesium, sodium or ammonium. The ethoxylated alkyl ether sulfate is generally present in the composition at a concentration of about 0 to about 20 wt. %, more preferably about 0.5 wt. % to 15 wt. %.

The ethoxylated alkyl ether sulfate may be made by sulfating the condensation product of ethylene oxide and C₈-10 alkanol, and neutralizing the resultant product. The ethoxylated alkyl ether sulfates differ from one another in the number of carbon atoms in the alcohols and in the number of moles of ethylene oxide reacted with one mole of such alcohol. Preferred ethoxylated alkyl ether polyethenoxy sulfates contain 12 to 15 carbon atoms in the alcohols and in the alkyl groups thereof, e.g., sodium myristyl (3 EO) sulfate.

Ethoxylated C₈-18 alkylphenyl ether sulfates containing from 2 to 6 moles of ethylene oxide in the molecule are also suitable for use in the invention compositions.

These detergents can be prepared by reacting an alkyl phenol with 2 to 6 moles of ethylene oxide and sulfating and neutralizing the resultant ethoxylated alkylphenol. The concentration of the ethoxylated alkyl ether sulfate surfactant is about 1 to about 8 wt. %.

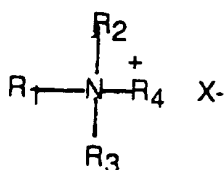
5 The ammonium, alkali metal or alkaline earth metal salt of the sulfonate surfactant is generally used in the instant compositions at a concentration of about 0 to 20 wt. %, more preferably about 0.5 wt. % to about 15 wt. %. Examples of suitable sulfonated anionic surfactants are the well known higher alkyl mononuclear aromatic sulfonates such as the higher alkyl benzene sulfonates containing from 10 to 16 carbon
10 atoms in the higher alkyl group in a straight or branched chain, C₈-C₁₅ alkyl toluene sulfonates and C₈-C₁₅ alkyl phenol sulfonates.

One of preferred sulfonates is linear alkyl benzene sulfonate having a high content of 3- (or higher) phenyl isomers and a correspondingly low content (well below 50%) of 2- (or lower) phenyl isomers, that is, wherein the benzene ring is preferably
15 attached in large part at the 3 or higher (for example, 4, 5, 6 or 7) position of the alkyl group and the content of the isomers in which the benzene ring is attached in the 2 or 1 position is correspondingly low. Particularly preferred materials are set forth in U.S. Patent 3,320,174.

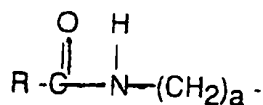
Other suitable anionic surfactants are the olefin sulfonates, including long-chain
20 alkene sulfonates, long-chain hydroxyalkane sulfonates or mixtures of alkene sulfonates and hydroxyalkane sulfonates. These olefin sulfonate detergents may be prepared in a known manner by the reaction of sulfur trioxide (SO₃) with long-chain olefins containing 8 to 25, preferably 12 to 21 carbon atoms and having the formula RCH=CHR₁ where R is a higher alkyl group of 6 to 23 carbons and R₁ is an alkyl group
25 of 1 to 17 carbons or hydrogen to form a mixture of sultones and alkene sulfonic acids which is then treated to convert the sultones to sulfonates. Preferred olefin sulfonates contain from 14 to 16 carbon atoms in the R alkyl group and are obtained by sulfonating an alpha-olefin.

Other examples of suitable anionic sulfonate surfactants are the paraffin sulfonates containing about 10 to 20, preferably about 13 to 17, carbon atoms. Primary paraffin sulfonates are made by reacting long-chain alpha olefins and bisulfites and paraffin sulfonates having the sulfonate group distributed along the paraffin chain are shown in U.S. Patents Nos. 2,503,280; 2,507,088; 3,260,744; 3,372,188; and German Patent 735,096.

The water-soluble zwitterionic surfactant (betaine), which is also generally present at a concentration of about 0 to 12 wt. %, preferably 0.5 wt. % to 10 wt. %, and provides good foaming properties and mildness to the present nonionic based liquid detergent. The zwitterionic surfactant is a water soluble betaine having the general formula:



wherein X is selected from the group consisting of CO_2^- and SO_3^- and wherein R_1 is an alkyl group having 10 to about 20 carbon atoms, preferably 12 to 16 carbon atoms, or the amido radical:



wherein R is an alkyl group having about 9 to 19 carbon atoms and a is the integer 1 to 4; R_2 and R_3 are each alkyl groups having 1 to 3 carbons and preferably 1 carbon; R_4 is an alkylene or hydroxyalkylene group having from 1 to 4 carbon atoms and, optionally, one hydroxyl group. Typical alkyldimethyl betaines include decyl dimethyl betaine or 2-(N-decyl-N, N-dimethyl-ammonia) acetate, coco dimethyl betaine or 2-(N-coco N, N-dimethylammonia) acetate, myristyl dimethyl betaine, palmityl dimethyl betaine, lauryl dimethyl betaine, cetyl dimethyl betaine, stearyl dimethyl betaine, etc.

The amidobetaines similarly include cocoamidoethylbetaine, cocoamidopropyl betaine and the like. A preferred betaine is coco ($\text{C}_8\text{-C}_{18}$) amidopropyl dimethyl betaine.

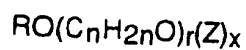
The instant compositions can also contain about 0 to about 10 wt. %, more preferably 0.5 wt. % to 8 wt. % of an alkyl polysaccharide surfactant or glucamide surfactant. The alkyl polysaccharides surfactants, which are used in conjunction with the aforementioned surfactant have a hydrophobic group containing from about 8 to about 20 carbon atoms, preferably from about 10 to about 16 carbon atoms, most preferably from about 12 to about 14 carbon atoms, and polysaccharide hydrophilic group containing from about 1.5 to about 10, preferably from about 1.5 to about 4, most preferably from about 1.6 to about 2.7 saccharide units (e.g., galactoside, glucoside, fructoside, glucosyl, fructosyl; and/or galactosyl units). Mixtures of saccharide moieties may be used in the alkyl polysaccharide surfactants. The number x indicates the number of saccharide units in a particular alkyl polysaccharide surfactant. For a particular alkyl polysaccharide molecule x can only assume integral values. In any physical sample of alkyl polysaccharide surfactants there will be in general molecules having different x values. The physical sample can be characterized by the average value of x and this average value can assume non-integral values. In this specification the values of x are to be understood to be average values. The hydrophobic group (R) can be attached at the 2-, 3-, or 4- positions rather than at the 1-position, (thus giving e.g. a glucosyl or galactosyl as opposed to a glucoside or galactoside). However, attachment through the 1- position, i.e., glucosides, galactoside, fructosides, etc., is preferred. In the preferred product the additional saccharide units are predominately attached to the previous saccharide unit's 2-position. Attachment through the 3-, 4-, and 6- positions can also occur. Optionally and less desirably there can be a polyalkoxide chain joining the hydrophobic moiety (R) and the polysaccharide chain. The preferred alkoxide moiety is ethoxide.

Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing from about 8 to about 20, preferably from about 10 to about 18 carbon atoms. Preferably, the alkyl group is a straight chain saturated alkyl group. The alkyl group can contain up to 3 hydroxy groups and/or the polyalkoxide chain can contain up to about 30, preferably less than about 10, alkoxide moieties.

Suitable alkyl polysaccharides are decyl, dodecyl, tetradecyl, pentadecyl, hexadecyl, and octadecyl, di-, tri-, tetra-, penta-, and hexagluco-
sides, galactosides, lactosides, fructosides, fructosyls, lactosyls, glucosyls and/or galactosyls and mixtures thereof.

5 The alkyl monosaccharides are relatively less soluble in water than the higher alkyl polysaccharides. When used in admixture with alkyl polysaccharides, the alkyl monosaccharides are solubilized to some extent. The use of alkyl monosaccharides in admixture with alkyl polysaccharides is a preferred mode of carrying out the invention. Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and pentagluco-
sides and tallow alkyl tetra-, penta-, and hexagluco-
sides.

The preferred alkyl polysaccharides are alkyl polyglucosides having the formula



wherein Z is derived from glucose, R is a hydrophobic group selected from the group consisting of alkyl, alkylphenyl, hydroxyalkylphenyl, and mixtures thereof in which said
15 alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14 carbon atoms; n is 2 or 3 preferably 2, r is from 0 to 10, preferable 0; and x is from 1.5 to 8, preferably from 1.5 to 4, most preferably from 1.6 to 2.7. To prepare these compounds a long chain alcohol (R_2OH) can be reacted with glucose, in the presence of an acid catalyst to form the desired glucoside. Alternatively the alkyl polyglucosides
20 can be prepared by a two step procedure in which a short chain alcohol (R_1OH) can be reacted with glucose, in the presence of an acid catalyst to form the desired glucoside. Alternatively the alkyl polyglucosides can be prepared by a two step procedure in which a short chain alcohol (C_{1-6}) is reacted with glucose or a polyglucoside ($x=2$ to 4) to yield a short chain alkyl glucoside ($x=1$ to 4) which can in turn be reacted with a longer
25 chain alcohol (R_2OH) to displace the short chain alcohol and obtain the desired alkyl polyglucoside. If this two step procedure is used, the short chain alkylglucoside content of the final alkyl polyglucoside material should be less than 50%, preferably less than 10%, more preferably less than about 5%, most preferably 0% of the alkyl polyglucoside.

The amount of unreacted alcohol (the free fatty alcohol content) in the desired alkyl polysaccharide surfactant is preferably less than about 2%, more preferably less than about 0.5% by weight of the total of the alkyl polysaccharide. For some uses it is desirable to have the alkyl monosaccharide content less than about 10%.

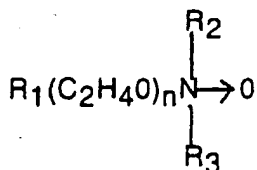
5 The used herein, "alkyl polysaccharide surfactant" is intended to represent both the preferred glucose and galactose derived surfactants and the less preferred alkyl polysaccharide surfactants. Throughout this specification, "alkyl polyglucoside" is used to include alkyl polyglycosides because the stereochemistry of the saccharide moiety is changed during the preparation reaction.

10 An especially preferred APG glycoside surfactant is Glucopon 625 ACSUP glycoside manufactured by the Henkel Corporation of Ambler, PA. APG25 is a nonionic alkyl polyglycoside characterized by the formula:



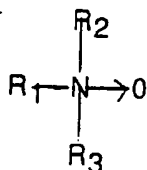
wherein $n=10$ (2%); $n=122$ (65%); $n=14$ (21-28%); $n=16$ (4-8%) and $n=18$ (0.5%) and x (degree of polymerization) = 1.6. APG 625 has: a pH of 6 to 12 (10% of APG 625 in distilled water); a specific gravity at 25°C of 1.1 g/ml; a density at 25°C of 9.1 lbs/gallon; a calculated HLB of 12.1 and a Brookfield viscosity at 35°C, 21 spindle, 5-10 RPM of 3,000 to 7,000 cps.

20 Amine oxide semi-polar nonionic surfactants comprise compounds and mixtures of compounds having the formula



25 wherein R_1 is an alkyl, 2-hydroxyalkyl, 3-hydroxyalkyl, or 3-alkoxy-2-hydroxypropyl radical in which the alkyl and alkoxy, respectively, contain from 8 to 18 carbon atoms, R_2 and R_3 are each methyl, ethyl, propyl, isopropyl, 2-hydroxyethyl, 2-hydroxypropyl, or 3-hydroxypropyl, and n is from 0 to 10. Particularly preferred are amine oxides of the
30 formula:

16



5

wherein R_1 is a C_{12-16} alkyl and R_2 and R_3 are methyl or ethyl. The above ethylene oxide condensates, amides, and amine oxides are more fully described in U.S. Pat. No. 4,316,824 which is hereby incorporated herein by reference. The concentration of the amine oxide in the instant compositions is 0 to 10 wt. %, more preferably 0.5 to 8 wt. % and most preferably 0.75 to 5 wt. %.

The instant composition can contain C_{12-14} alkyl monoalkanol amide such as lauryl/myristyl monoalkanol amide (LMMEA) and/or a C_{12-14} alkyl dialkanol amide such as lauryl diethanol amide (LDEA) or coco diethanol amide or an ethoxylated alkanol amide, wherein the concentration of the alkyl monoalkanol amide or alkyl dialkanol amide or ethoxylated alkanol amide is 0 to 5 wt. %, more preferably 0.5 wt. % to 4.0 wt. %.

The instant compositions contain about 0 wt. % to about 12 wt. %, more preferably about 1 wt. % to about 10 wt. %, of at least one solubilizing agent which can be sodium xylene sulfonate, sodium cumene sulfonate, a C_{2-3} mono or dihydroxy alkanols such as ethanol, isopropanol and propylene glycol and mixtures thereof. The solubilizing agents are included in order to control low temperature cloud clear properties. Urea can be optionally employed in the instant composition as a supplemental solubilizing agent at a concentration of 0 to about 10 wt. %, more preferably about 0.5 wt. % to about 8 wt. %.

Other solubilizing agents are water soluble sodium salts of C_1-C_3 substituted benzene sulfonate hydrotropes such as sodium cumene sulfonate or sodium xylene sulfonate and glycerol, water-soluble polyethylene glycols having a molecular weight of 300 to 600, polypropylene glycol of the formula $HO(CH_2CHCH_2O)_nH$ wherein n is a number from 2 to 18, mixtures of polyethylene glycol and polypropylene glycol (Synalox) and mono C_1-C_6 alkyl ethers and esters of ethylene glycol and propylene glycol having the structural formulas $R(X)_nOH$ and $R_1(X)_nOH$ wherein R is C_1-C_6 alkyl

30

group. R₁ is C₂-C₄ acyl group. X is (OCH₂CH₂) or (OCH₂(CH₃)CH) and n is a number from 1 to 4.

Representative members of the polypropylene glycol include dipropylene glycol and polypropylene glycol having a molecular weight of 200 to 1000, e.g., polypropylene glycol 400. Other satisfactory glycol ethers are ethylene glycol monobutyl ether (butyl cellosolve), diethylene glycol monobutyl ether (butyl carbitol), triethylene glycol monobutyl ether, mono, di, tri propylene glycol monobutyl ether, tetraethylene glycol monobutyl ether, mono, di, tripropylene glycol monomethyl ether, propylene glycol monomethyl ether, ethylene glycol monohexyl ether, diethylene glycol monohexyl ether, propylene glycol tertiary butyl ether, ethylene glycol monoethyl ether, ethylene glycol monomethyl ether, ethylene glycol monopropyl ether, ethylene glycol monopentyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monopropyl ether, diethylene glycol monopentyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, triethylene glycol monopropyl ether, triethylene glycol monopentyl ether, triethylene glycol monohexyl ether, mono, di, tripropylene glycol monoethyl ether, mono, di tripropylene glycol monopropyl ether, mono, di, tripropylene glycol monopentyl ether, mono, di, tripropylene glycol monohexyl ether, mono, di, tributylene glycol mono methyl ether, mono, di, tributylene glycol monoethyl ether, mono, di, tributylene glycol monopropyl ether, mono, di, tributylene glycol monobutyl ether, mono, di, tributylene glycol monopentyl ether and mono, di, tributylene glycol monohexyl ether, ethylene glycol monoacetate and dipropylene glycol propionate.

The liquid cleaning composition contains about 10 to 3000 ppb (parts per billion), more preferably about 100 to 1,400 ppb of a blue or violet dye which is preferably a fluorescent violet dye such as external D&C violet No. 2 which is an alizarine violet dye having a Cl# of 60730 (monosodium salt of 2-[(9,10 dihydro-4-hydroxy-9, 10-Dioxo-1-anthracenyl)amino]-5-methyl-benzen sulfonic acid] manufactured by the Hitton Davis Co. The balance of the liquid cleaning composition is water.

The instant formulas explicitly exclude alkali metal silicates and alkali metal builders such as alkali metal polyphosphates, alkali metal carbonates, alkali metal phosphonates and alkali metal citrates because these materials, if used in the instant composition, would cause the composition to have a high pH as well as leaving residue on the surface being cleaned.

In final form, the instant liquid compositions exhibit stability at reduced and increased temperatures. More specifically, such compositions remain clear and stable in the range of 5°C to 50°C, especially 10°C to 43°C. The instant compositions have a light transmission of at least 95%. Such compositions exhibit a pH of 5 to 8. The liquid compositions are readily pourable and exhibit a viscosity in the range of 100 to 600 cps as measured at 25°C. with a Brookfield RVT Viscometer using a #2 spindle rotating at 30 RPM. Preferably, the viscosity is maintained in the range of 300 to 500 cps. The instant compositions have a minimum foam height of 110 mls after 55 rotation at 40°C as measured by the foam volume test using 0.75 grams of the composition per liter of water and 1 gram of corn oil per liter of water having a hardness of 300 ppm.

The container is preferably a thermoplastic bottle formed from PET resin by a conventional blow molding process. The thermoplastic can contain 0 to about 1 wt. %, more preferably about 0.1 wt. % to about 0.75 wt. % of a blue dye such as Blue Toner 88-048-5 manufactured by Color Matrix Corp.

The following examples illustrate the filled package of the container and liquid cleaning composition of the described invention. Unless otherwise specified, all percentages are by weight. The exemplified compositions are illustrative only and do not limit the scope of the invention. Unless otherwise specified, the proportions in the examples and elsewhere in the specification are by weight.

Example 1

The following composition in wt. % was prepared by simple mixing procedure at 25°C.

	A	B	C
Neodol 1-9	19	19	19
Ammonium lauryl sulfate	6	6	6
MgSO ₄ (7H ₂ O)	1.0	1.0	1.0
Sodium formate	2.0	2.0	2.0
LMMEA	2.0	2.0	2.0
LDEA	2.0		
Cocoamido propyl betaine	5.0	5.0	5.50
Sodium xylene sulfonate	1.2	1.2	1.2
Sodium formate	2.0	2.0	2.0
Perfume	0.2	0.2	0.2
HEDTA	0.083	0.083	0.083
Na Bisulfate	--	0.05	--
D&C violet #2 (ppb)	1200	1200	--
Water	Bal.	Bal.	Bal.

5

Example 2

The following formulas (in wt. %) were prepared by simple mixing at 25°C and filled into a blue tint bottle.

	A	B	C	D	E
NH ₄ AEOS (1.3EO)	15.0	15.0	15.0	15.0	15.0
Neodol 1-9	15.0	15.0	15.0	15.0	15.0
Cocoamido propyl betaine	4.5	4.5	4.5	4.5	4.5
APG625	4.5	4.5	4.5	4.5	4.5
Lauryl/myristyl monoethanol amide	3.0	3.0	3.0	3.0	3.0
Sodium xylene sulfonate	1.85	1.85	1.85	1.85	1.85
Urea	1.5	1.5	1.5	1.5	1.5
Sodium formate	1.1	1.1	1.1	1.1	1.1
MgSO ₄ (7H ₂ O)	0.75	0.75	0.75	0.75	0.75
Perfume	0.35	0.35	0.35	0.35	0.35
D&C violet #2 (ppb)	450	924	1032	1398	0
Water	Bal.	Bal.	Bal.	Bal.	Bal.
Tristimulus values liquid in blue tint bottle	79.656	71.713	68.873		82.157
X	85.314	76.633	73.500		80.388
Y	82.157	80.388	78.621		79.413
Z					
Chromaticity coordinate values liquid in blue tint bottle	0.3223	0.3135	0.3117		0.3047
X	0.3452	0.3350	0.3326		0.3243
Y					

The chromaticity coordinate values of A to E are all within the previously defined values of container and fluid.

What Is Claimed:

1. A filled package comprising:
 - (a) a transparent container having chromaticity coordinate values of x from about 0.3080 to 0.3240 and y from about 0.3280 to about 0.3430; and
 - 5 (b) a liquid cleaning composition disposed in said container, said liquid cleaning composition comprising:
 - (1) about 0.05 wt. % to about 50 wt. % of at least one surfactant;
 - (2) 10 to 3000 ppb of a blue or violet dye; and
 - (3) the balance being water, wherein said liquid cleaning composition
- 10 has chromaticity coordinate values of x from about 0.3080 to about 0.3240 and y from about 0.3280 to about 0.3430, wherein the filled package of the liquid cleaning composition disposed in the transparent container has chromaticity coordinate values of x from about 0.3100 to about 0.3200 and y from about 0.3300 to about 0.3400.
2. A filled package according to Claim 1, wherein at least one said surfactant
- 15 is selected from an ethoxylated alkyl ether sulfate surfactant, an alkyl sulfate surfactant, a zwitterionic surfactant, a sulfonate surfactant, an alkyl glucoside surfactant, an alkyl polyglucoside surfactant, a glucamide surfactant, an amine oxide surfactant and a nonionic surfactant having an ethylene oxide group and mixtures thereof.
3. A filled package according to Claim 1, wherein said at least one surfactant
- 20 comprises a mixture of a nonionic surfactant having ethylene oxide groups, an ethoxylated alkyl ether sulfate surfactant, a zwitterionic surfactant and an alkyl polyglucoside surfactant.
4. A filled package according to Claim 3 further includes an alkyl monoalkanol amide and/or an alkyl dialkanol amide.
- 25 5. A filled package according to Claim 1 further including urea.
6. A filled package according to Claim 1, wherein said dye in said liquid cleaning composition is a fluorescent blue or violet dye.

7. A filled package according to Claim 1, wherein said transparent container is formed from a thermoplastic resin selected from the group consisting of polyethylene terephthalate, polystyrene, polyethylene and polyvinyl chloride.
8. A filled package according to Claim 7, wherein said container contains a
5 blue or violet dye uniformly mixed in said thermoplastic resin.

INTERNATIONAL SEARCH REPORT

Inter. Application No
PC1/US 97/00812A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/40 C11D17/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 44 15 159 C (HENKEL KGAA) 16 March 1995 see page 2, line 1 - page 4, line 12; claims 1-11 ---	1-3,6
A	US 4 278 538 A (LAWRENCE HOPETON S ET AL) 14 July 1981 see column 4, line 64 - column 9, line 51; figures 1-6 ---	
A	US 5 451 342 A (DESAI SURESHCHANDRA G) 19 September 1995 see the entire document ---	4
A	US 3 935 129 A (JABALEE WALTER J) 27 January 1976 cited in the application see the entire document ---	5
	--- -/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search

10 April 1997

Date of mailing of the international search report

22.04.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Ainscow, J

INTERNATIONAL SEARCH REPORT

International Application No
PCI/US 97/00812

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 4 822 854 A (CIOLINO LAURA A) 18 April 1989 see column 1, line 7 - column 2, line 46 -----</p>	7,8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/00812

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 4415159 C	16-03-95	WO 9529977 A	09-11-95
US 4278538 A	14-07-81	NONE	
US 5451342 A	19-09-95	AU 6818594 A	20-12-94
		BR 9406654 A	06-02-96
		CN 1124974 A	19-06-96
		WO 9428097 A	08-12-94
US 3935129 A	27-01-76	NONE	
US 4822854 A	18-04-89	CA 1338733 A	26-11-96

THIS PAGE BLANK (USPTO)